Neutron and X-Ray reflectometry studies of planar interfaces for power sources

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Motivation

Hi, my name is Bob. I'm a battery and your guide on this poster.

Today, rapid development of portable electronic devices (*Fig.1*) and green energy (*Fig.2*) leads to the need of modernization of existing and development of new power sources.

All main parameters (*specific capacity, life time, safety, charge time*) depend on the processes (*solid electrolyte interface (SEI) formation, Li deposition*) taking place on buried interfaces (Fig.3 [1])

Figure 1. The variety of different portable electronic devices.

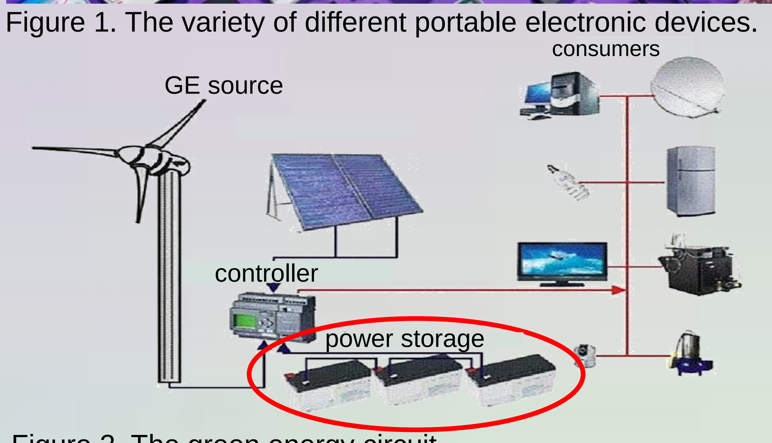
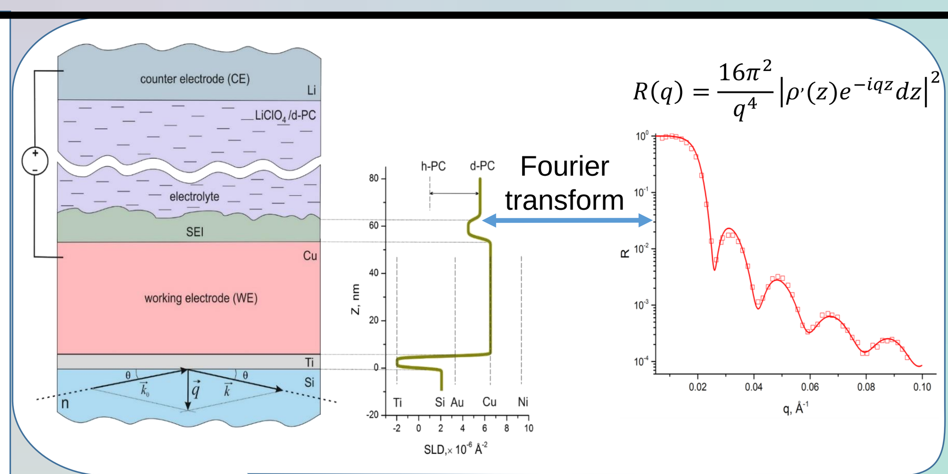


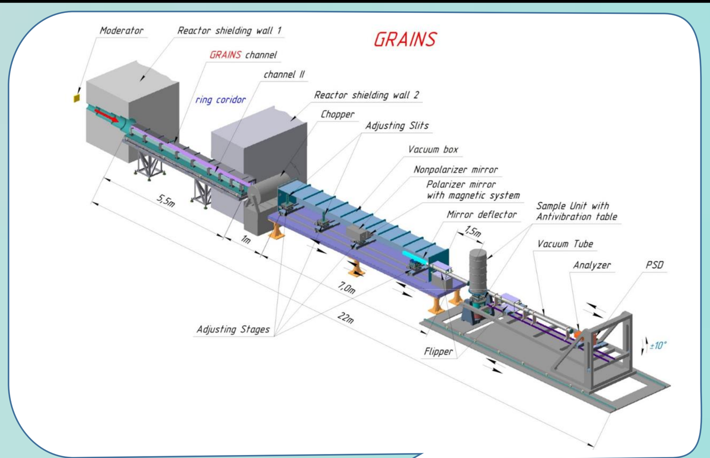
Figure 2. The green energy circuit.

Figure 3. Buried interfaces in Li-Ion battery.

Reflectometry



$$R(q) = \frac{16\pi^2}{q^4}\left|\int \rho'(z)e^{-iqz}dz\right|^2$$



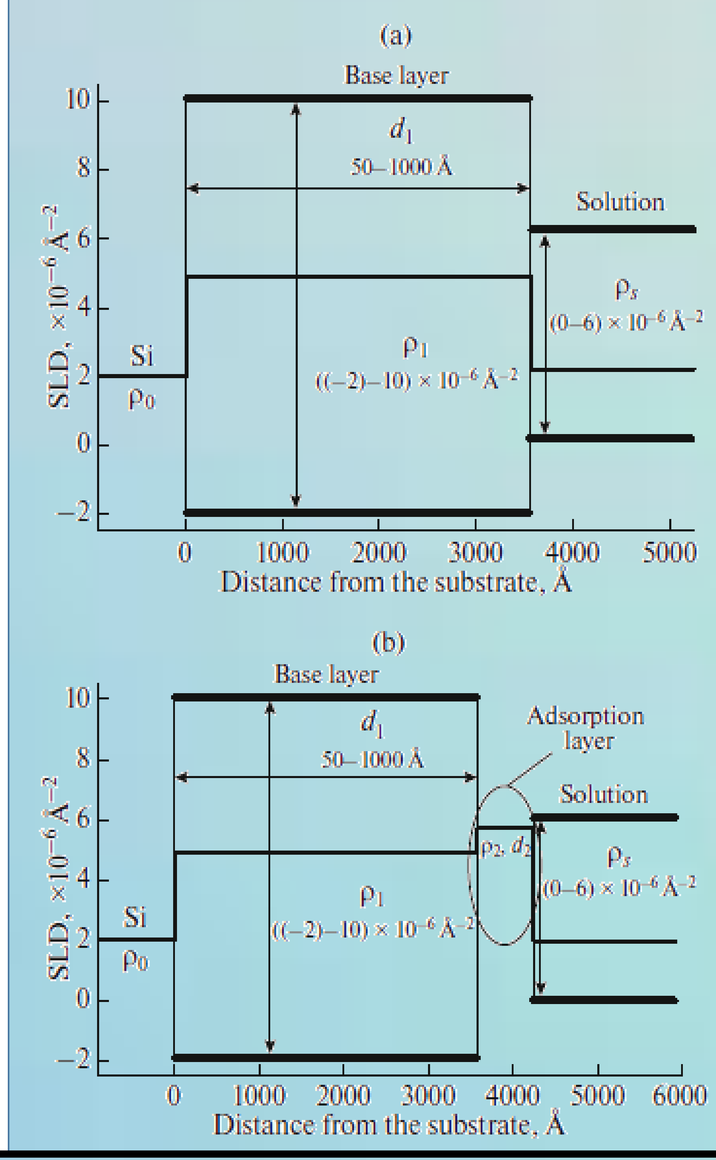
In neutron reflectometry experiment beam of neutrons comes thru the substrate, reflects from each interface and forms an interference picture on the detector (*reflectometry curve*) that corresponds a Fourier transform of the scattering length density profile (*SLD*).

Neutron reflectometry is a perfect method to study buried interfaces in situ/operando because of high neutron penetration rate.

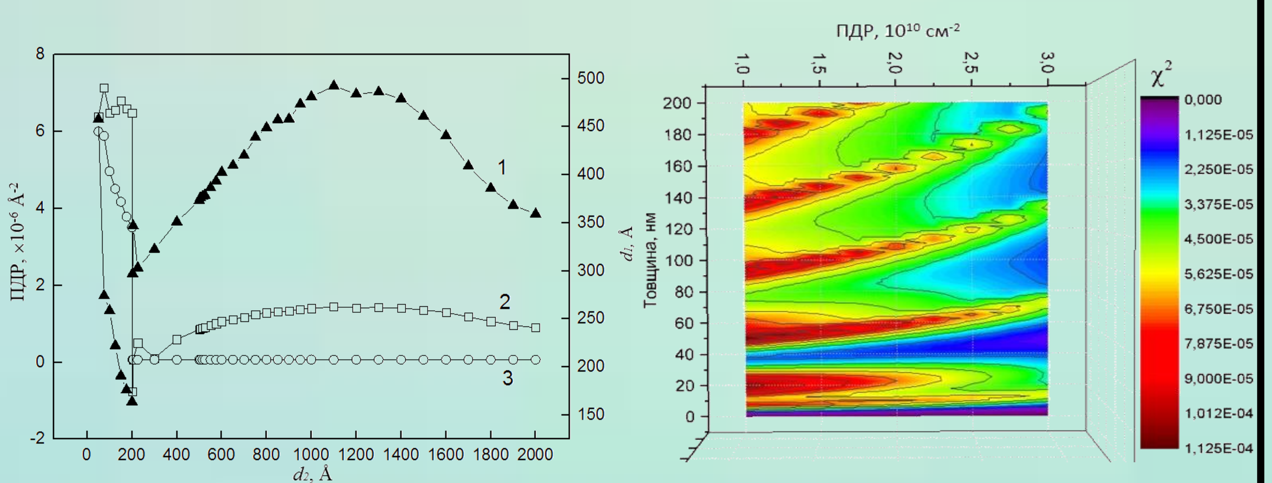
Contrast variation experiments may highlight a range of interest (*ROI*).

But, sometimes optimization of initial sample should be done to increase sensitivity of method to ROI.

Sample optimization



$$\chi^2 = \frac{\int dq_z[R_2(q_z,\rho_0,\rho_1,\rho_2,\rho_s,d_1,d_2) - R_1(q_z,\rho_0,\rho_1,\rho_s,d_1)]^2}{\int dq_z[R_1(q_z,\rho_0,\rho_1,\rho_s,d_1)+B]^2}$$



Thin adsorption layer (up to 200 Å):
- Electrode SLD ≈ 6 * 10^{-6}Å^{-2} (Cu);
- Electrode thickness ≈ 450 Å;
- Deuterated electrolyte.

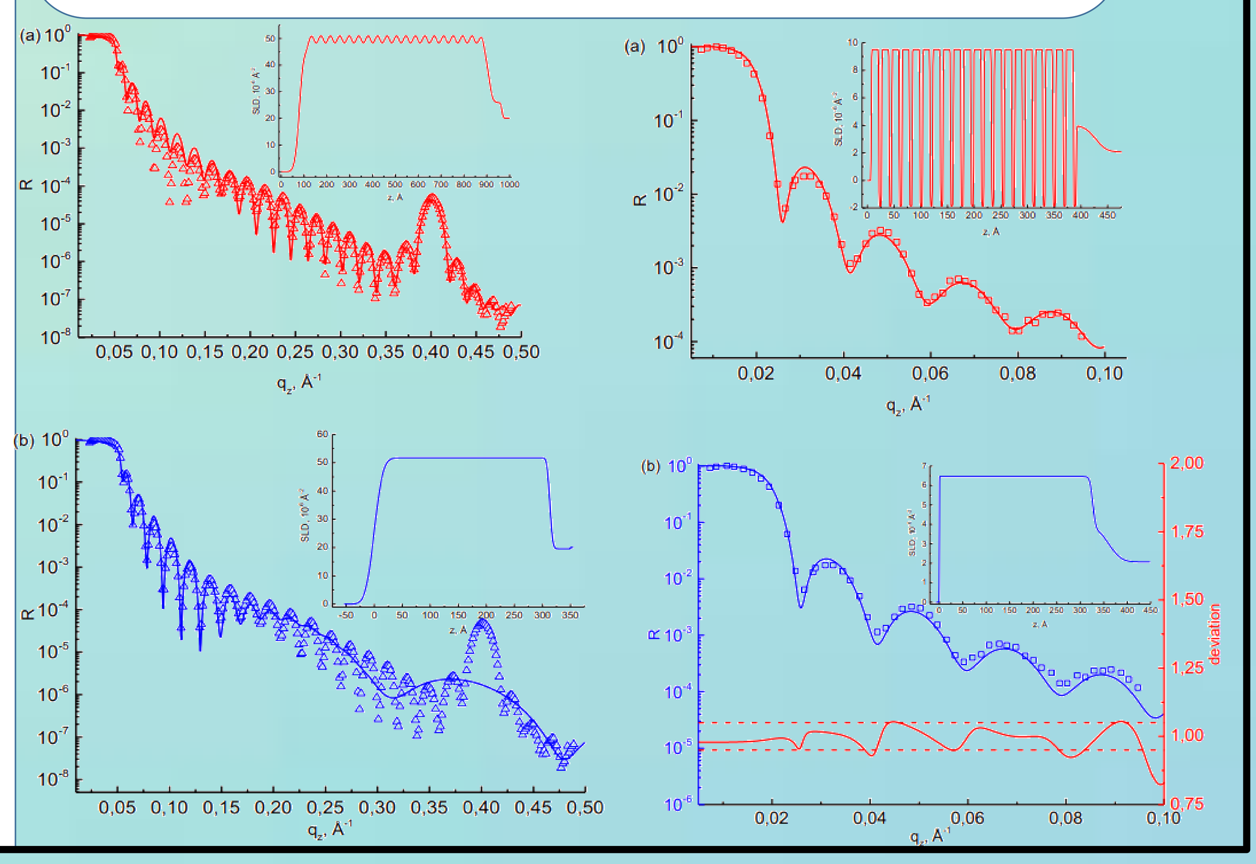
Thick adsorption layer (over 200 Å):
- Electrode SLD ≈ 1 * 10^{-6}Å^{-2} (Li, Na, ???);
- Electrode thickness ≈ 450 Å;
- Protonated electrolyte.

Briefly, optimization of initial sample was done by maximization of χ^2 value. Two working regimes of SEI layer could be highlighted. For more info, please, look at [2,3].

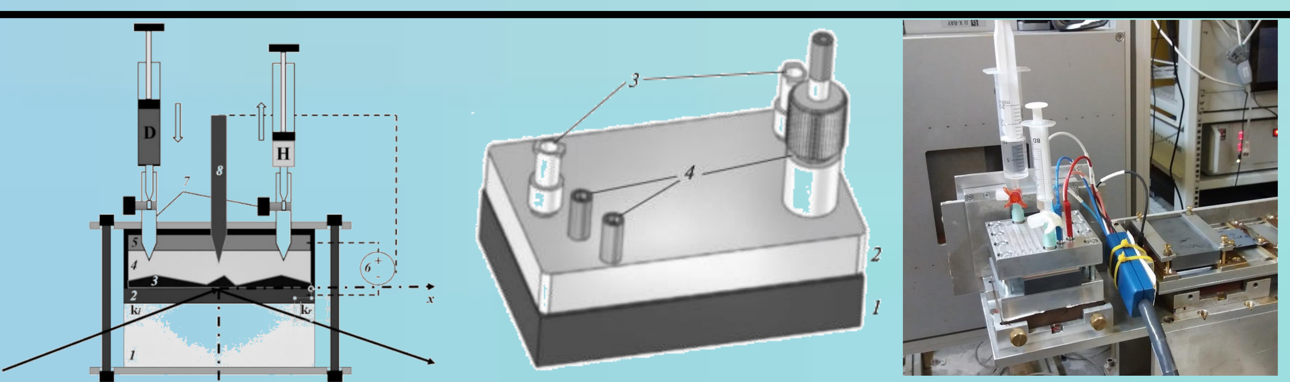
Multilayered substrate

In [4] is shown that Ti/Ni multilayers could be used as a layer with a variable SLD. In the beginning range of momentum transfer values reflectivity curves could be approximated with a multilayer or with a monolayer (*with mean SLD by volume*) model.

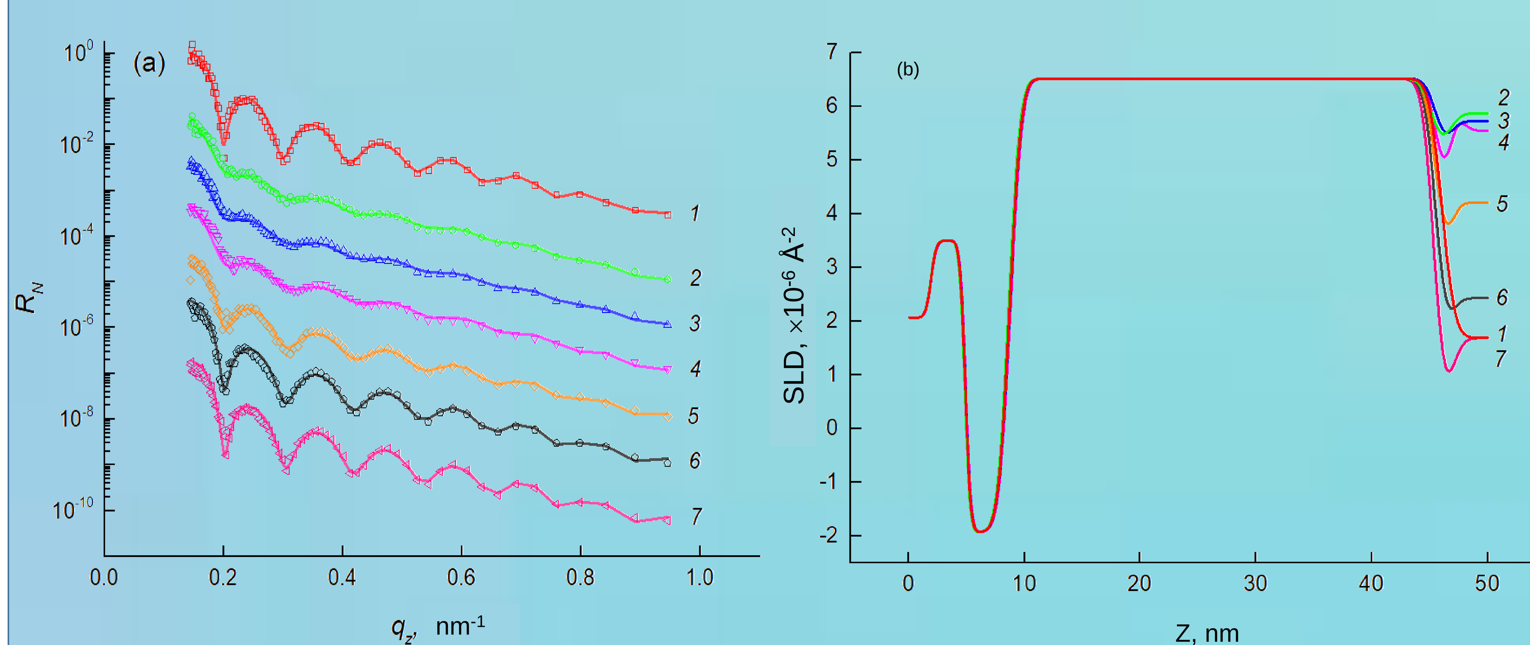
Left – X-Ray reflectometry, right – neutron reflectometry.



Contrast variation

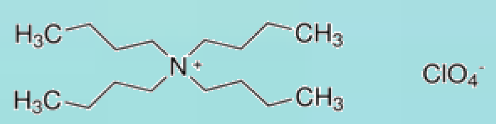


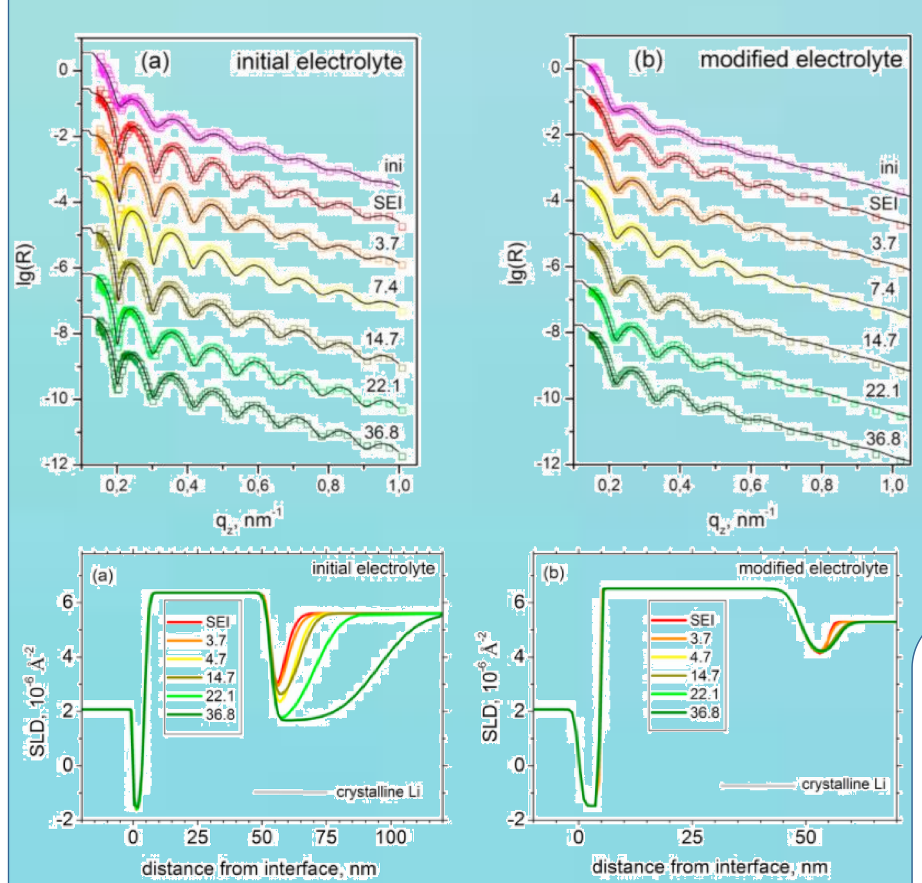
Bro, what they did to you?!

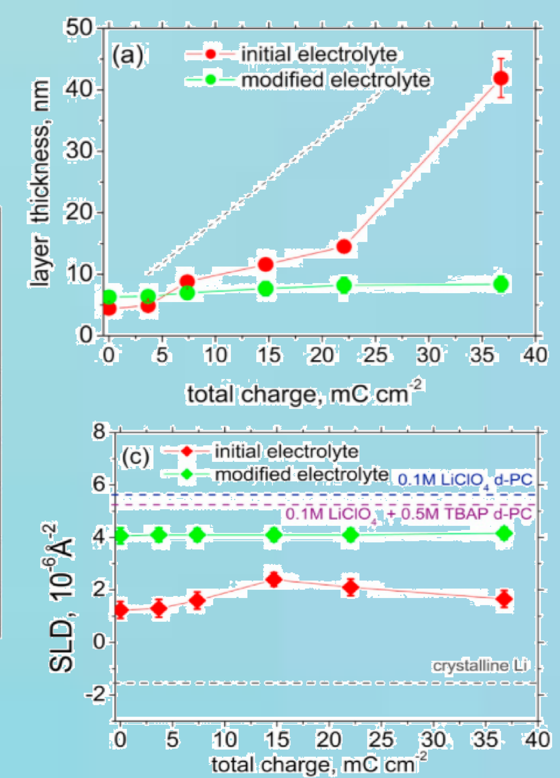


By variation of contrast of the 0.5 M $LiClO_4$ in 1:1 EC:DMC electrolyte solution non-uniform SEI with thickness 1 nm was detected [5].

Electrolyte modification







In [6] electrolyte was modified by **TBAP** to prevent non-uniform Li deposition. However, TBA+ ions strongly suppress Li migration.

Conclusions

- Sensitivity of neutron reflectometry (NR) in studies of planar interfaces for lithium power sources can be regulated and enhanced by varying the scattering contrasts between interface components. Optimal interfaces configurations were determined for studies of thin (thickness < 20 nm) and thick (thickness > 20 nm) SEI layers. Multilayers were tested for quasi-continuous variation of electrode SLD based on data of neutron and X-ray reflectometry.
- Specialized cell for NR experiments with liquid electrolytes was developed. The contrast variation experiments based on H/D substitution in liquid electrolyte confirmed ability of the method to detect layers with thickness down to 1 nm;
- Modification of electrolyte with TBAP leads to strong suppression of Li migration.

References:
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